Crystal Structures † and Spectroscopic Properties of the Polymeric Adducts formed from Cu(CN) and Cu(NCS) with 2,9-Dimethyl-1,10-phenanthroline

Giorgio Oscar Morpurgo*
Istituto di Chimica Generale e Inorganica, Università di Roma, 00185 Roma, Italy
Giulia Dessy and Vincenzo Fares
Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, C.N.R., Area della Ricerca di Roma, Via Salaria Km. 29, 00016 Monterotondo Stazione, Italy

The crystal structures of the title adducts, [{Cu(dmphen)(CN)}$_n$] (1) and [{Cu(dmphen)(NCS)}$_n$] (2) (dmphen = 2,9-dimethyl-1,10-phenanthroline), consist of one-dimensional zigzag chains of tetrahedral copper(I) atoms linked by cyanide and thiocyanate groups, respectively. Stacks of dmphen molecules are formed by the 'fitting' of centrosymmetrical polymeric sequences. Complex (1) crystallizes in space group $P2_1/n$ with cell dimensions, a = 9.839(4), b = 7.788(2), c = 16.559(7) Å, β = 92.33(4)°, and Z = 4; (2) crystallizes in space group *Pbca*, with cell dimensions, a = 16.283(3), b = 9.485(2), c = 18.115(3) Å, and Z = 8. Polarization properties of the i.r. and electronic bands have been determined. Chain formation affects the vibration and bending modes within the zigzag system. In the optical spectrum of both the complexes two bands have been detected: one charge-transfer from d_{yz} of copper to φ_9 (lowest unoccupied molecular orbital of dmphen), polarized along the short axis (z) of each [Cu(dmphen)]$^+$ mono-complex, and another from d_{z^2} or $d_{x^2-y^2}$ of copper to φ_9, plane-polarized (xy) because of some vibronic or electronic coupling mechanism operating between the above mentioned mono-complexes stacked in the 'fitted' polymeric sequences.

A large number of copper(I) complexes exhibit intense optical absorption due to metal-to-ligand charge-transfer (m.l.c.t.) transitions. In the photoexcited state the metal can participate in numerous redox reactions, some of which also have potential practical applications.[1] Although extensive studies have been reported on the mechanism of the intramolecular electron transfer induced by irradiating monomeric copper species in solution, very little work has been performed on photoactive copper(I) insoluble polymers. Taking advantage of the fact that (*i*) non-chelating ambidentate ligands such as CN$^-$ and NCS$^-$ are capable of bridging metal nuclei to form zigzag or helical chains,[2-6] (*ii*) both Cu(CN) and Cu(NCS) form addition compounds with many nitrogen bases,[7] and (*iii*) 2,9-dimethyl-1,10-phenanthroline (dmphen) is a particularly suitable base as its complex with copper(I), [Cu(dmphen)$_2$]$^+$, can be excited in its low-lying m.l.c.t. region giving rise to photoluminescence,[8] we have succeeded in producing copper(I) polymers with low-lying c.t. bands. The structure and spectroscopic characterization of the two-dimensional coordination polymers [{Cu(dmphen)(CN)}$_n$] and [{Cu(dmphen)(NCS)}$_n$], having a stacked layer arrangement, are the subject of the present report. A study of their photochemical properties is in progress and will be presented in the near future.

Experimental

Materials.—The chemicals were commercial products; 2,9-dimethyl-1,10-phenanthroline (dmphen) from C. Erba was used without further purification.

Crystal Preparations.—[{Cu(dmphen)(CN)}$_n$] (1) was obtained by reacting equimolar amounts of Cu(CN) and dmphen in water. The initial white suspension turned brown-red with time. The crude powder, after being separated by centrifuging, was washed with water, dried in a desiccator, and recrystallized from hot dimethyl sulphoxide (dmso). The complexes [Cu(dmphen)X] (X = NCS, Cl, Br, I, or N$_3$) were prepared according to the method described for [Cu(phen)(NCS)] (phen = 1,10-phenanthroline; ref. 9); [{Cu(dmphen)(NCS)}$_n$] (2) was recrystallized from hot dmso.

Spectroscopic Measurements.—Powder reflectance spectra were measured with a Beckman DK-1A spectrophotometer equipped with a standard reflectance unit. Single-crystal polarized spectra were recorded on a Shimadzu MPS-50L spectrophotometer, equipped with a microscope. I.r. polarized spectra were measured with a Perkin-Elmer 580 B spectrophotometer on small crystals secured in a 'mosaic' fashion on a CsBr disc by use of Nujol. The i.r. spectra of (1) were of good quality, those of (2) of a lesser standard, especially where Nujol bands and compound bands overlapped.

Crystal Data.—($C_{15}H_{12}CuN_3$)$_n$ (1), M = 297.82, red-orange monoclinic crystals, a = 9.839(4), b = 7.788(2), c = 16.559(7) Å, β = 92.33(4)°, U = 1 267.9(9) Å^3, D_m = 1.55(1) g cm^{-3} (by flotation), Z = 4, D_c = 1.56 g cm^{-3}, $F(000)$ = 608, Cu-K_α radiation, λ = 1.541 8 Å, graphite monochromator, μ(Cu-K_α) = 23.48 cm^{-1}, space group $P2_1/n$ (C_{2h}^5, no. 14) (equivalent position x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) from systematic absences.

($C_{15}H_{12}CuN_3S$)$_n$ (2), M = 329.88, red-orange orthorhombic crystals, a = 16.283(3), b = 9.485(2), c = 18.115(3) Å, U = 2 798(1) Å^3, D_m = 1.56(1) g cm^{-3} (by flotation), Z = 8; D_c = 1.57 g cm^{-3}, $F(000)$ = 1 344, Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, μ(Mo-K_α) = 17.44 cm^{-1}, space group *Pbca* (D_{2h}^{15}, no. 61) from systematic absences.

X-*Ray Data Collection.*—Plate-like crystals, 0.3 × 0.2 × 0.05 mm for (1), and 0.4 × 0.3 × 0.15 mm for (2), were used for the data collection on a $P2_1$ Syntex automated four-circle

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† *Supplementary data available* (No. SUP 23846, 25 pp.): structure factors, anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for [{Cu(dmphen)(CN)}$_n$] (1)

Atom	*X/a*	*Y/b*	*Z/c*
Cu	1 394(2)	1 697(2)	1 881(1)
N(1)	1 675(11)	3 945(13)	2 457(6)
N(2)	824(8)	2 253(11)	661(5)
N(3)	−679(9)	899(12)	1 838(5)
C(1)	2 316(12)	5 025(15)	2 760(7)
C(2)	1 581(11)	2 906(12)	111(6)
C(3)	1 040(15)	3 289(20)	−692(7)
C(4)	−318(13)	3 035(18)	−860(7)
C(5)	−1 154(12)	2 344(16)	−284(7)
C(6)	−532(10)	1 972(14)	491(6)
C(7)	−1 346(10)	1 233(13)	1 101(6)
C(8)	−2 708(12)	925(16)	951(8)
C(9)	−3 348(13)	1 380(19)	169(8)
C(10)	−2 571(14)	2 063(18)	−414(8)
C(11)	−3 469(14)	161(19)	1 570(9)
C(12)	−2 772(14)	−240(19)	2 295(8)
C(13)	−1 397(13)	152(16)	2 405(7)
C(14)	−575(15)	−200(17)	3 201(8)
C(15)	3 064(14)	3 233(18)	323(8)

Table 2. Atomic co-ordinates (× 10^4), with e.s.d.s in parentheses for [{Cu(dmphen)(NCS)}$_n$] (2)

Atom	*X/a*	*Y/b*	*Z/c*
Cu	284(1)	2 239(1)	1 681(1)
S	−922(1)	2 821(2)	2 294(1)
N(1)	−550(4)	5 375(7)	2 944(4)
N(2)	1 237(3)	3 681(6)	1 586(3)
N(3)	217(4)	2 628(6)	554(3)
C(1)	−689(4)	4 347(8)	2 669(4)
C(2)	1 356(4)	4 109(7)	880(4)
C(3)	796(4)	3 549(8)	337(4)
C(4)	870(5)	4 007(9)	−412(4)
C(5)	1 503(6)	4 962(10)	−595(5)
C(6)	2 032(6)	5 460(10)	−105(4)
C(7)	1 980(5)	5 055(9)	665(5)
C(8)	2 480(6)	5 564(9)	1 221(6)
C(9)	2 363(5)	5 152(10)	1 918(6)
C(10)	1 731(4)	4 225(8)	2 096(4)
C(11)	285(6)	3 498(11)	−910(4)
C(12)	−287(6)	2 594(9)	−681(4)
C(13)	−304(5)	2 130(8)	59(4)
C(14)	−965(7)	1 059(10)	332(6)
C(15)	1 573(6)	3 696(11)	2 909(5)

Table 3. Bond distances (Å) and angles (°), with e.s.d.s in parentheses for [{Cu(dmphen)(CN)}$_n$] (1)

Cu–N(1)	2.008(11)	Cu–N(2)	2.121(9)
Cu–N(3)	2.131(9)	Cu–C(1^{I})	1.897(12)
N(1)–C(1)	1.15(2)	N(2)–C(2)	1.30(1)
N(2)–C(6)	1.37(1)	N(3)–C(7)	1.39(1)
N(3)–C(13)	1.33(2)	C(2)–C(3)	1.44(2)
C(2)–C(15)	1.51(2)	C(3)–C(4)	1.37(2)
C(4)–C(5)	1.39(2)	C(5)–C(6)	1.43(2)
C(6)–C(7)	1.44(2)	C(7)–C(8)	1.38(2)
C(8)–C(9)	1.46(2)	C(8)–C(11)	1.42(2)
C(9)–C(10)	1.36(2)	C(11)–C(12)	1.39(2)
C(12)–C(13)	1.39(2)	C(13)–C(14)	1.54(2)
N(1)–Cu–N(2)	107.5(4)	N(1)–Cu–N(3)	112.6(4)
N(1)–Cu–C(1^{I})	111.9(5)	N(2)–Cu–N(3)	79.1(3)
N(2)–Cu–C(1^{I})	125.9(4)	N(3)–Cu–C(1^{I})	116.0(4)
Cu–N(1)–C(1)	154.8(10)	Cu–C(1)–N(1)	169.6(9)
Cu–N(2)–C(6)	112.3(7)	C(2)–N(2)–C(6)	119.9(9)
Cu–N(3)–C(7)	113.2(7)	C(7)–N(3)–C(13)	117.2(9)
N(2)–C(2)–C(3)	121.6(10)	N(2)–C(2)–C(15)	118.6(10)
C(3)–C(2)–C(15)	119.8(10)	C(2)–C(3)–C(4)	118.5(11)
C(3)–C(4)–C(5)	121.1(11)	C(4)–C(5)–C(6)	116.8(10)
N(2)–C(6)–C(5)	122.0(9)	C(5)–C(6)–C(7)	118.8(9)
N(3)–C(7)–C(8)	123.4(10)	C(6)–C(7)–C(8)	120.8(10)
C(7)–C(8)–C(9)	120.0(11)	C(7)–C(8)–C(11)	118.6(11)
C(8)–C(9)–C(10)	119.3(12)	C(5)–C(10)–C(9)	121.9(12)
C(8)–C(11)–C(12)	117.4(12)	C(11)–C(12)–C(13)	120.4(13)
N(3)–C(13)–C(14)	113.9(11)	C(12)–C(13)–C(14)	123.1(12)

Symmetry code: I $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 4. Bond distances (Å) and angles (°) with e.s.d.s in parentheses for [{Cu(dmphen)(NCS)}$_n$] (2)

Cu–S	2.323(2)	C(3)–C(4)	1.430(10)
Cu–N(1^{I})	1.943(6)	C(4)–C(5)	1.411(13)
Cu–N(2)	2.076(6)	C(4)–C(11)	1.398(12)
Cu–N(3)	2.078(6)	C(5)–C(6)	1.324(13)
S–C(1)	1.644(8)	C(6)–C(7)	1.449(13)
N(1)–C(1)	1.117(10)	C(7)–C(8)	1.382(13)
N(2)–C(2)	1.356(9)	C(8)–C(9)	1.335(14)
N(2)–C(10)	1.329(9)	C(9)–C(10)	1.391(11)
N(3)–C(3)	1.344(9)	C(10)–C(15)	1.577(11)
N(3)–C(13)	1.322(10)	C(11)–C(12)	1.332(13)
C(2)–C(3)	1.442(10)	C(12)–C(13)	1.412(11)
C(2)–C(7)	1.410(11)	C(13)–C(14)	1.560(13)
S–Cu–N(1^{I})	103.7(2)	C(3)–C(4)–C(5)	118.6(7)
S–Cu–N(2)	121.0(2)	C(3)–C(4)–C(11)	116.7(7)
S–Cu–N(3)	112.5(2)	C(4)–C(5)–C(6)	123.1(8)
N(1^{I})–Cu–N(2)	117.5(2)	C(5)–C(6)–C(7)	120.8(9)
N(1^{I})–Cu–N(3)	121.1(2)	C(2)–C(7)–C(6)	118.5(8)
N(2)–Cu–N(3)	80.8(2)	C(2)–C(7)–C(8)	116.4(8)
Cu–S–C(1)	102.2(3)	C(7)–C(8)–C(9)	120.2(9)
Cu^{I}–N(1)–C(1)	174.0(4)	C(8)–C(9)–C(10)	120.6(8)
Cu–N(2)–C(2)	112.5(4)	N(2)–C(10)–C(9)	122.1(7)
C(2)–N(2)–C(10)	116.9(6)	N(2)–C(10)–C(15)	115.3(7)
Cu–N(3)–C(2)	111.5(4)	C(9)–C(10)–C(15)	122.6(7)
C(3)–N(3)–C(13)	119.0(6)	C(4)–C(11)–C(12)	119.9(8)
S(1)–C(1)–N(1)	177.6(7)	C(11)–C(12)–C(13)	120.7(8)
N(2)–C(2)–C(3)	116.3(6)	N(3)–C(13)–C(12)	121.3(7)
N(2)–C(2)–C(7)	123.6(7)	N(3)–C(13)–C(14)	117.5(7)
C(3)–C(2)–C(7)	120.1(7)	C(12)–C(13)–C(14)	121.2(8)
N(3)–C(3)–C(2)	118.9(6)		
N(3)–C(3)–C(4)	122.3(6)		
C(2)–C(3)–C(4)	118.8(7)		

Symmetry code: I $x, \frac{1}{2} + y, \frac{1}{2} - z$.

diffractometer. The cell dimensions were obtained by least-squares refinement of the setting angles for 15 reflections. The intensities of 942 independent reflections for (1) and 1 279 for (2), having $I \geqslant 3\sigma(I)$, recorded by the θ—2θ scan technique, were used for the structure determination *via* Patterson and Fourier methods, and for the refinement. Data were corrected for Lorentz and polarization effects but not for absorption, given the low value of μ and the size of crystals. Atomic co-ordinates were refined by block-diagonal least squares to a final conventional R of 0.056 for (1) and 0.045 for (2), with the weighting scheme $w = (\sin\theta)/\lambda$. Anisotropic thermal parameters were used for all non-hydrogen atoms and a fixed isotropic value of 4.5 Å^2 for the hydrogen atoms, included at calculated positions. Computations were performed on a Univac 1108 computer at Rome University. Tables 1 and 2 give the positional parameters of the atoms and their standard deviations within the chemical units. Bond distances and angles are listed in Tables 3 and 4. Figures 1 and 2 show the packing of polymeric sequences projected on ($\bar{1}01$) for (1) and the ($\bar{1}0\bar{1}$) plane for (2). Such projections coincide with the crystal face on which light-polarized spectra have been measured.

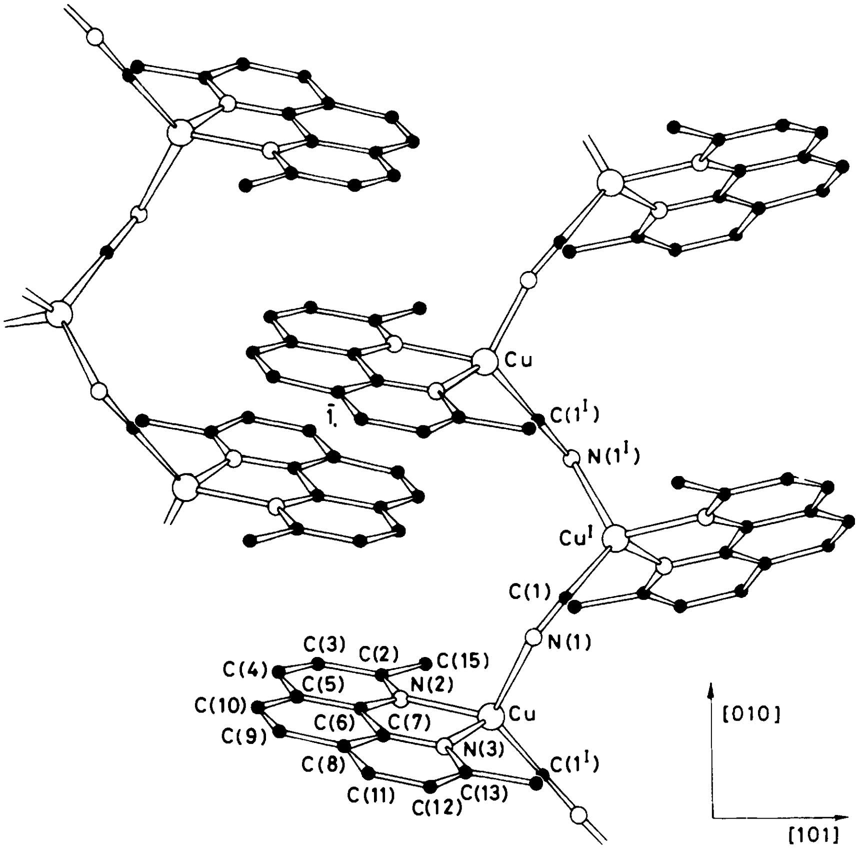

Figure 1. Projection of the structure of [{Cu(dmphen)(CN)}$_n$] (1) on the ($\bar{1}$01) plane. Roman numeral superscripts are defined in Table 3

Results and Discussion

Description of the Structure of (1).—Apart from the discrete $[Cu(CN)_4]^{3-}$ tetrahedra of $K_3[Cu(CN)_4]$ (ref. 4), the other copper(I) cyanide complexes of known structure show Cu(CN) chains connected by organic ligands or CN^- groups, to form two- or three-dimensional polymeric networks.[2,3,5] Owing to the chelating features of dmphen, the crystal structure of (1), already briefly reported,[10] consists of infinite non-linked zigzag chains of Cu(CN). The copper atom has four neighbours in a distorted tetrahedron, formed by the nitrogen [N(1)] and carbon [C(1^I)] atoms from two, symmetrically related bridging CN^- groups, and by two nitrogen atoms [N(2) and N(3)] from dmphen (Figure 1). The result is a one-dimensional polymeric structure developing along the [010] direction. Each polymeric sequence is ' fitted ' with its centrosymmetrical one so that stacks of aromatic systems are formed with alternate dmphen interplanar distances of 3.26 and 3.90 Å each dmphen molecule forming an angle of 23° with the (010) plane. Due (presumably) to steric or packing effects, the Cu–C–N–Cu^I sequence is not linear, the –N– and –C– angles being 154.8(10) and 169.6(9)° respectively. The Cu–C, Cu–N, and C–N distances of 1.897(12), 2.008(11), and 1.15(2) Å respectively agree well both with those found in other tetrahedral CuN_3C complexes, such as [Cu(CN)(pydz)] (pydz = pyridazine), [Cu(CN)(cpy)] (cpy = 4-cyanopyridine), and $[Cu(CN)(N_2H_4)]$,[11,5] where the sequence does not deviate much from linearity (angular range 173—179°), and with those found in the polymeric anion, $[\{Cu_2(CN)_4\}_n]^{2-}$ of $[Cu_3(en)_2(CN)_4]\cdot H_2O$ (en = ethylenediamine) where a larger deviation from linearity is present,[12] the angles ranging from 160 to 175°.

Description of the Structure of (2).—Figure 2 shows the crystal and molecular structure of (2). It is related to that of (1) as: (*i*) NCS^- groups act as a bridge between two metal atoms; (*ii*) the dmphen molecules tend to couple by facing each other; and (*iii*) simple relationships between the unit-cell dimensions are found [$a(2) \simeq c(1)$; $b(2) > b(1)$; $c(2) \simeq 2a(1)$]. The copper atom environment has a distorted tetrahedral geometry, the angles around Cu ranging from 81 to 121° (Table 4). The tetrahedron apices are occupied by two nitrogen atoms of one dmphen ligand and by sulphur and nitrogen atoms from two different symmetrically related NCS^- groups to form a CuN_3S unit. Complex (2) also has a one-dimensional polymeric structure developing along the [010] direction. It can be compared with other Cu^I thiocyanate complexes such as $[\{Cu(NCS)(PMePh_2)_2\}_2]$ or polymeric $[\{Cu(NCS)\}_n]$.[11,13-15] The Cu–S distance of 2.323(2) Å is a little shorter than that found in the above mentioned polymeric compounds, where it ranges from 2.344(2) to 2.367(2) Å, but where the co-ordination sphere around copper is S_3N or S_2N_2. The value of 1.943(6) Å for the Cu–N(thiocyanate) distance as well as each bond distance within the thiocyanate group are similar to those found for other Cu(NCS) complexes [1.92(1)—2.01(3) Å].[11,14,15] The Cu–N(dmphen) bond distance of 2.077(6) Å is a little longer than that found for $[Cu(dmphen)_2]ClO_4$ of 2.053(6) Å,[16] but significantly shorter than that of 2.126(9) Å found in (1); this might be connected with the net positive charge of the copper atom, being larger for the cationic bis(phenanthroline) compound.

We finally consider the characteristic common feature of (1) and (2) due to the stacking at about the same distance of the pairs of dmphen planes. The fitting between the centrosymmetric chains is apparently different in the two structures as the overlap, as viewed along *b*, of each couple of dmphen

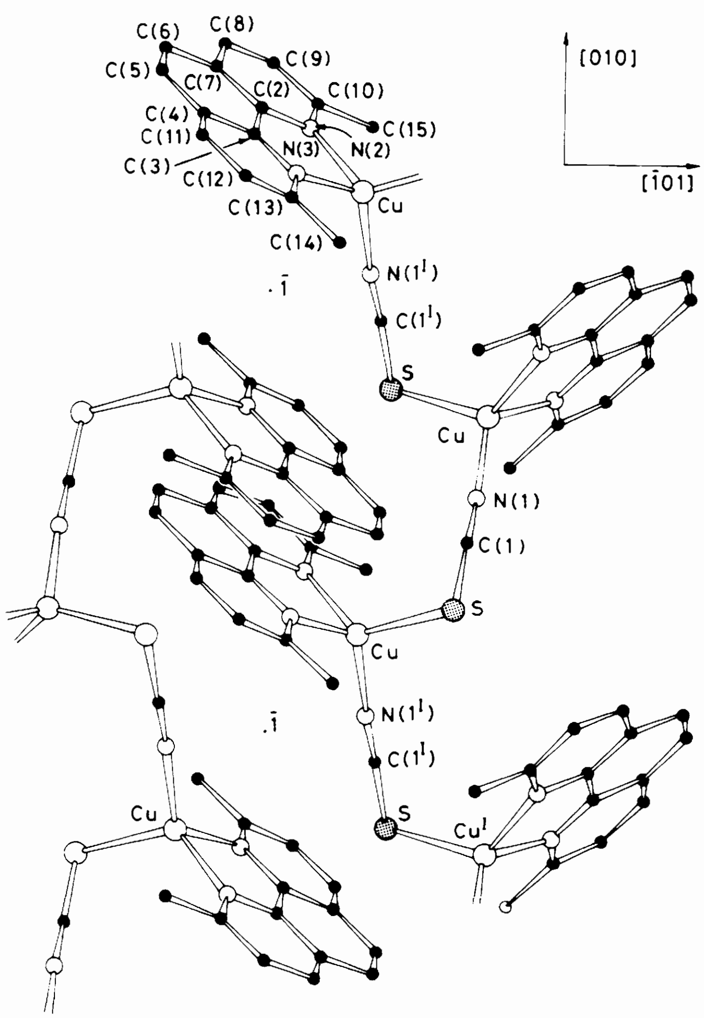

Figure 2. Projection of the structure of $[\{Cu(dmphen)(NCS)\}_n]$ (2) on the $(\bar{1}0\bar{1})$ plane. Roman numeral superscripts are defined in Table 4

molecules accounts for 40% of total dmphen area in (1) and only for *ca.* 15% in (2) due to the greater inclination of the dmphen molecular plane respect to the (010) plane. However small, the overlap could be one of the main stabilizing factors of these structures.

Infrared Spectra.—Figure 3 shows the i.r. spectra of a solution of dmphen and the polarized spectra of (1) and (2) measured with light entering perpendicular to the $(\bar{1}01)$ and $(\bar{1}0\bar{1})$ planes respectively and with the electric vector vibrating along the directions indicated in Figures 1 and 2.

The part of the spectrum of (1) due to dmphen can be interpreted in terms of C_{2v} symmetry, with B_2 transitions polarized along b, and A_1 modes activated in the other direction. Most of the bands of the spectrum of (2) appear with mixed polarization as the dmphen plane is inclined with respect to the (010) plane. The frequencies of some bands of (1) and (2), their correlations, and probable assignments are reported in Table 5.

The position of the bands assigned to the C–N stretching modes of the anions is consistent with CN^- and NCS^- acting as bidentate ligands, while the multiplicity and polarization of the transitions are related to the formation of zigzag polymers. The two transitions at 2 085 and 2 096 cm^{-1} in the spectrum of (1) can be associated to vibrations similar to the A_g and B_g skeletal modes of polyethylene [17] (a zigzag molecule with line group D_{2h}), once the proper line group is taken into account (Table 6). The C–S stretching vibration of (2) is also consistent with metal-nitrogen and metal-sulphur bonding as it appears as a multiplet between the zone where *N*-bonded (780—850 cm^{-1}) and *S*-bonded (690–720 cm^{-1}) thiocyanate absorbs.[6] The main reason for assigning the 440 cm^{-1} band of (1) to the symmetric Cu–N(dmphen) stretching vibration is its polarization. The other assignments are consistent with the literature data indicated in Table 5. The ν(Cu–S) mode could not be identified.

Electronic Spectra.—Figure 4 shows the polarized crystal spectra at room temperature of (1) and (2) in the region 14 000—25 000 cm^{-1} with polarized light in the directions

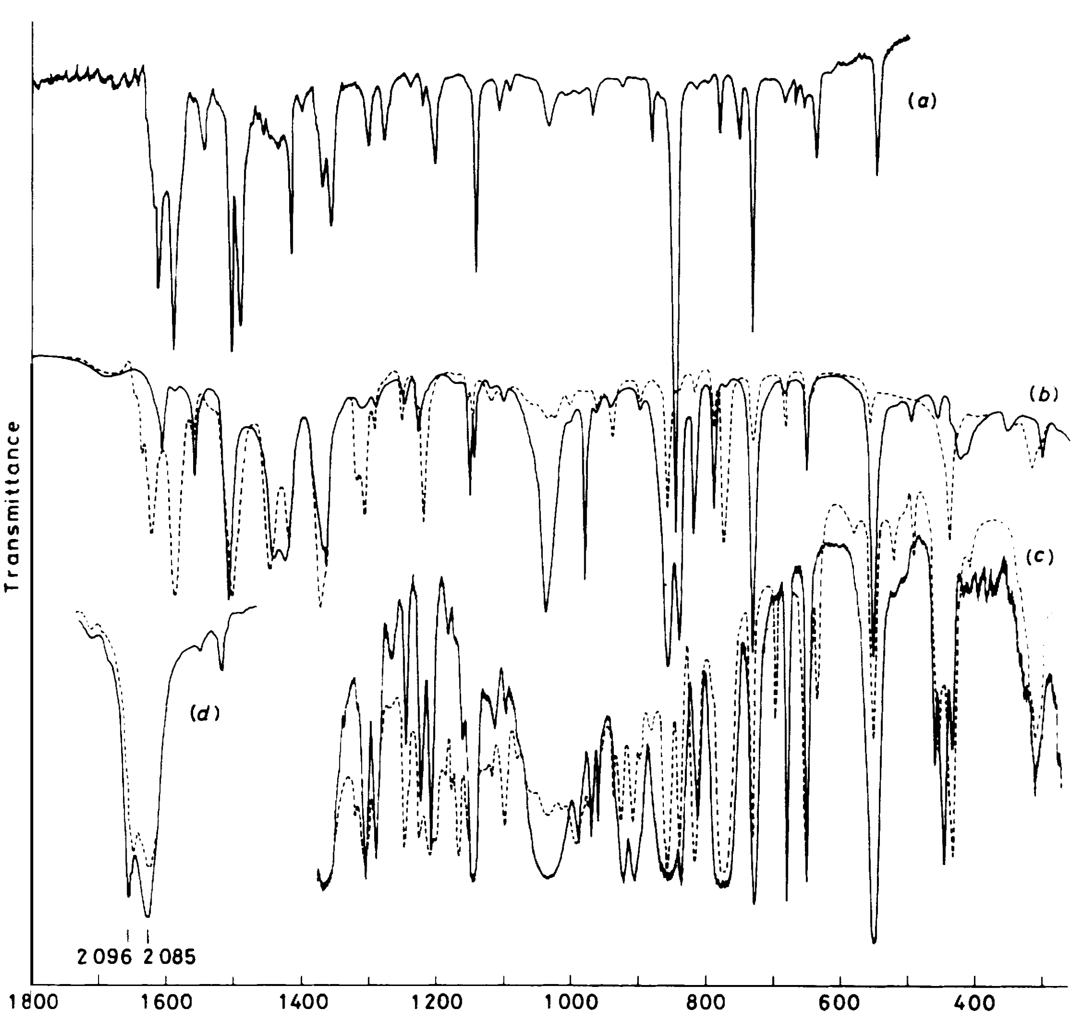

Figure 3. I.r. spectra of (*a*) $CHCl_3$ and CS_2 solutions of dmphen; (*b*) the $(\bar{1}01)$ crystal plane of complex (1) in polarized light (solid ine = electric vector parallel to [010]; broken line = electric vector parallel to [101]); (*c*) the $(\bar{1}0\bar{1})$ crystal plane of complex (2) (solid ine = electric vector parallel to [010]; broken line = electric vector parallel to $[\bar{1}01]$); and (*d*) C–N stretching frequency region of complex (1)

already mentioned. The spectrum of (1) is composed of two bands, one with mixed polarization at 23 500 cm^{-1} and another 19 000 cm^{-1} polarized perpendicular to [010], in the [Cu(dmphen)]$^+$ plane, along the short axis of this group. The latter band is obtained by subtracting the 23 500 cm^{-1} absorbance from that measured in the other direction. In the case of (2) the mixed-polarized component of the spectrum is the band with a maximum at 23 200 cm^{-1}, while that along the short axis of [Cu(dmphen)]$^+$ is at 20 500 cm^{-1} (shoulder at 19 500 cm^{-1}). These bands are considered to be m.l.c.t.[8,18,19] The short axis polarized band is related to the $d_{yz} \longrightarrow \varphi_9$ transition (*a*, in C_{2v}; φ_9 = lowest unoccupied molecular orbital of dmphen).[19] Its lower energy in solid cyanide relative to thiocyanate reflects the lower competition of the former anion for copper(I) electrons. The splitting of *ca.* 1 000 cm^{-1} among the vibronic components [the vibrational structure in the spectrum of (1) has been tentatively indicated by vertical bars in Figure 4], also common to [Cu(dmphen)$_2$]$^+$ (ref. 8), suggests a vibronic coupling with ring deformation modes possibly corresponding to the i.r. A_1 band at 770 cm^{-1}. The complex [Fe(phen)$_3$]$^{2+}$ shows, at difference, a splitting of about 1 500 cm^{-1} (ref. 19), the frequency of symmetric C–C and C–N stretching modes, as a consequence of a larger contribution of polar structures in the excited state.

The assignment of the high-energy transition is assisted by dmso solution spectra. From conductivity measurements and visible spectra (Figure 5) it appears that while [Cu(dmphen)X] compounds (X = Cl, Br, I, or NCS; N_3^- behaves as CN^-) ionize to give the [Cu(dmphen)$_2$]$^+$ chromophore, this is not the case for (1). In addition, the slightly more soluble species related to (1), prepared with 2,2′-biquinoline in place of dmphen, shows its high-energy band intensity to be linearly dependent on concentration.[20] Apparently the high-energy band, which (1) in dmso is at 26 000 cm^{-1}, reflects the stacking of [Cu(dmphen)]$^+$ mono-complexes as it occurs in the solid, where they form a molecular arrangement of

Table 5. Infrared frequencies (cm^{-1}) for complexes (1) and (2) [all the bands of (2) are mixed-polarized unless otherwise stated]

(1)	Mode	(2)	Mode	Assignment	Ref.
2 096 2 085	Mixed	2 124 2 120 2 100 2 060		C–N(CN, NCS) stretch	*a*, *b*
1 635, 1 590 1 510 1 505	A_1 B_2 A_1	1 625, 1 580 1 515 1 500		ring stretch C–C and C–N	*b*, *c*, *d*
		936, 910 900, 870		first overtone (N–C–S) bend	*b*, *e*
860, 842	B_2	858, 840		out of plane C–H bend heteroatom ring	*b*, *f*, *g*
815 790	B_2 B_2	815 790 (sh)	 B_2	out of plane C–H bend carbocyclic ring	*b*, *f*, *g*
770	A_1			ring stretch (breathing)	
		770—780		C–S stretch	6
730	B_2	730		out of plane C–H bend carbocyclic ring	*b*, *f*, *g*
		464, 455 449, 435		(N–C–S) bend	*b*, *f*
440	A_1	441	A_1	symmetric Cu–N(dmphen) stretch	*h*, *i*
425	B_2			Cu–C(CN) stretch	*h*, *j*
318, 302	Mixed	310		Cu–N(CN,NCS) stretch	*e*

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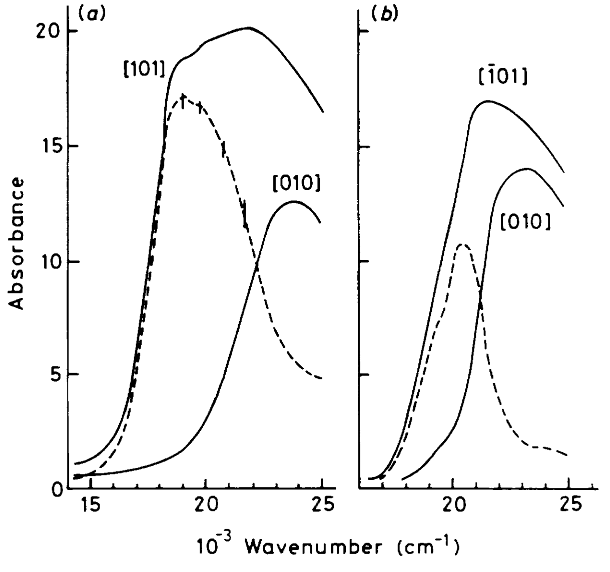

Figure 4. Polarized crystal spectra (arbitrary units) of: (*a*) complex (1) and (*b*) complex (2). Polarization directions are specified near each curve. Dotted curves represent the difference between the solid lines

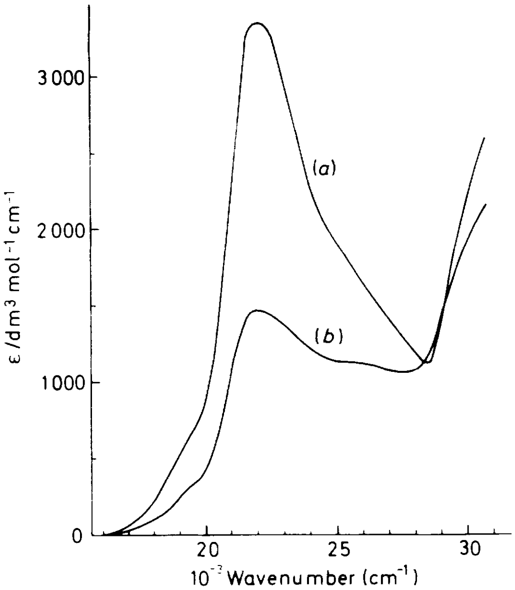

Figure 5. Spectra of dmso solutions of (*a*) [Cu(dmphen)Cl] and (*b*) complex (1)

approximately C_{2h} symmetry. If the band at 23 500 cm^{-1} in the solid corresponds to that at 26 000 cm^{-1} and if it is considered that the electron transferred to the ligand comes from a metal orbital more stable than d_{yz}, then the transition concerned is the d_{z^2} or $d_{x^2-y^2} \longrightarrow \varphi_9$ (b_2 in C_{2v}) charge transfer, perpendicularly polarized (y) in each isolated [Cu(dmphen)]$^+$,

Table 6. Correlation table

Isolated chain (line group)		Isolated chain within the unit cell	Unit-cell space group of (1)
D_{2h} $(C_2 = y)$	C_2 $(C_2 = y)$	C_1	C_{2h} $(C_2 = x)$
A_g	$A(z)$	$A(xyz)$	$A_u(x)$
B_{1g}	$B(xy)$		$B_u(yz)$

coupled through some electronic or vibrational mechanism to that of the other molecule, to become polarized in the *yz* plane.

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